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<p>(21) International Application Number: PCT/EP96/03977 (22) International Filing Date: 6 September 1996 (06.09.96) (30) Priority Data: 95306300.5 8 September 1995 (08.09.95) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: CLARK, Michael, Thomas; Thornton Research Centre, Pool Lane, Ince, Chester CH1 3SH (GB). VERKOUW, Hendrik, Tijmen; Sittingbourne Research Centre, Broad Oak Road, Sittingbourne, Kent ME9 8AG (GB).</p>		<p>(81) Designated States: AU, BR, CA, CN, HU, JP, KR, RU, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: ALKENYL-SUBSTITUTED DICARBOXYLIC ACID OR ANHYDRIDE ESTER DERIVATIVES (57) Abstract Alkenyl-substituted dicarboxylic acid or anhydride ester derivatives, useful as dispersant additives in lubricating oil compositions, having an alkenyl group derived from an atactic propylene oligomer substantially of formula (I), where n is in the range 15 to 120, having number average molecular weight (M_n) in the range 700 to 5000, and molar ratio dicarboxylic acid or anhydride moieties:atactic propylene oligomer in the range 1:1 to 2:1, and having an ester group derived from a polyol; a process for their preparation; and lubricating oil compositions and concentrates containing them.</p> <div style="text-align: right; margin-top: 20px;"> $\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\ & & \\ \text{H} - (\text{CH} - \text{CH}_2)_n - \text{C} = \text{CH}_2 \end{array} \quad (\text{I})$ </div>		

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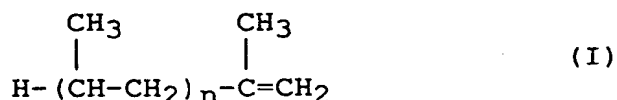
ALKENYL-SUBSTITUTED DICARBOXYLIC ACID OR
ANHYDRIDE ESTER DERIVATIVES

The present invention relates to alkenyl-substituted dicarboxylic acid or anhydride ester derivatives, particularly to such derivatives useful as dispersant additives in lubricating oil compositions, to their preparation and to lubricating oil compositions and concentrates containing them.

GB-A-981850 discloses as oil additives esters of polyisobutenylsuccinic acids which are obtained by reaction of polyisobutenylsuccinic acids with a polyol, e.g. pentaerythritol. These products have become established as dispersant additives for lubricating oils, being of the dispersant type often being referred to as "ashless" because of the absence of a metal component.

It has now surprisingly been found that by using a particular class of polyolefins it is possible to prepare alkenyl ester dispersant additives for lubricating oils displaying improved dispersancy properties when compared with the conventional esters described hereinabove.

According to the present invention there are thus provided alkenyl-substituted dicarboxylic acid or anhydride ester derivatives, useful as dispersant additives in lubricating oil compositions, having an alkenyl group derived from an atactic propylene oligomer substantially of the formula



where n is in the range 15 to 120, having number average molecular weight (M_n) in the range 700 to 5000.

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and molar ratio dicarboxylic acid or anhydride moieties : atactic propylene oligomer in the range 1:1 to 2:1, and having an ester group derived from a polyol.

Such atactic propylene oligomers may conveniently
5 be prepared as described in EP-B-0490454 which is hereby fully incorporated by reference.

The number average molecular weight (M_n) of the atactic propylene oligomer is determined by
10 quantitative reaction with ozone on the assumption that each oligomer chain contains one double bond, as will be readily understood by those skilled in the art.

The upper value of 5000 for M_n of the atactic propylene oligomer is due to the fact that molecular weights above 5000 can give handling problems in
15 preparation of the alkenyl ester derivatives from the atactic propylene oligomer due to viscosity levels. The lower value of 700 for the M_n is because low molecular weight products tend to be less effective as dispersants.

20 Preferably, the alkenyl group is derived from an atactic propylene oligomer of formula I, which has n in the range 15 to 70 and M_n in the range 700 to 3000, and more preferably n in the range 20 to 60 and M_n in the range 900 to 2500.

25 The polyol suitably comprises an alkane polyol for instance an alkylene diol or polyalkylene polyol.

Suitable alkane polyols comprise alkane polyols having at least two and preferably at least four hydroxy groups such as the trihydroxyalkanes, e.g.
30 ethylene glycol, propylene glycol, polymethylene glycols, trihydroxybutanes, pentanes, hexanes, heptanes, octanes, nonanes, dodecanes, etc., as well as tetrahydroxy alkanes, pentahydroxy alkanes, hexahydroxy alkanes, and the sugar alcohols such as erythritol,
35 pentaerythritol, tetritols, pentitols, hexitols, mannitol, sorbitol, sucrose, glucose and the like.

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Preferred polyols comprise pentaerythritol, glycerol, sorbitol and sucrose, or mixtures of two or more thereof, more preferably glycerol and sorbitol, or a mixture thereof.

5 In accordance with the invention, the alkenyl ester derivatives of the invention may be prepared by a process which comprises reacting an alkenyl-substituted dicarboxylic acid or anhydride with a polyol, both of which have been defined above.

10 The molar ratio of alkenyl-substituted dicarboxylic acid or anhydride to polyol used in the present process may vary between wide limits. Suitably, the molar ratio of alkenyl-substituted dicarboxylic acid or anhydride to polyol is in the range 0.5:1 to 10:1, preferably
15 0.6:1 to 3:1. The reaction temperature may also vary between wide limits with reaction temperatures in the range 150 to 250 °C being suitable and in the range 180 to 210 °C being preferred. The reaction time may also vary between wide limits with reaction times in the
20 range 6 to 30 hours being suitable and in the range 18 to 24 hours being preferred. A solvent may be present in the reaction mixture. Suitable examples of solvents include hydrocarbons e.g. xylene, toluene and mineral oil; ethers e.g. diphenylether; ketones; and
25 chlorobenzene. An esterification catalyst may also be added. Conventional esterification catalysts may be used. Suitable esterification catalysts include mineral acids, sulphonic acids and BF_3 , mineral acids being preferred. Water vapour which is produced during the
30 reaction can be removed from the reaction zone as the reaction proceeds, by application of methods well known in the art. Suitably, the reaction is carried out in a closed reaction vessel.

35 The alkane polyols may suitably be mixed with an amine, prior to their reaction with one or more alkylene oxides.

Suitable amines comprise amino-alcohols, polyoxyalkylene polyamines and hydroxyamines. Preferably, the amine is an amino-alcohol.

5 The molar ratio of dicarboxylic acid or anhydride groups : to polyol groups in the derivatives of the present invention is preferably in the range 0.5:1 to 10:1, more preferably in the range 0.6:1 to 3:1.

10 The dicarboxylic acid is suitably derived from an alpha-beta unsaturated dicarboxylic acid, anhydride or ester, such as maleic, fumaric, itaconic, etc.; maleic acid and anhydride being particularly preferred, in which case the dicarboxylic acid grouping in the present product is thus a succinic acid derivative.

15 The alkenyl-substituted dicarboxylic acid is preferably derived by reacting an alpha-beta unsaturated dicarboxylic acid with the atactic propylene oligomer as described hereinabove.

20 The alkenyl-substituted dicarboxylic acid or anhydride may be prepared according to established procedures from atactic propylene oligomer as defined above of required molecular weight and an appropriate amount of the dicarboxylic acid or anhydride. Thus, the atactic propylene oligomer may be contacted with for instance maleic acid or anhydride at a temperature of 25 140 to 220 °C, optionally in the presence of chlorine, e.g. as described in e.g. GB-A-949981. The proportions of atactic propylene oligomer and maleic anhydride and also chlorine, when used, are selected so as to yield the desired MALA/alkenyl group ratio in the final 30 product. Another method for the preparation of polyolefin-substituted succinic anhydride is described in US-A-3172892, according to which a halogenated, in particular chlorinated, alkenyl group is reacted with maleic anhydride.

35 From e.g. NL-A-7412057 it is known to prepare hydrocarbon-substituted succinic anhydride by thermally

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reacting an alkenyl group with maleic anhydride, a procedure which may be combined with that of GB-A-949981, as is illustrated in GB-A-1440219 and GB-A-1543627. The products prepared in this way include
5 compounds in which the alkenyl chain is connected to the alpha and/or beta carbon atoms of the succinic group.

Preferably, the atactic propylene oligomer is reacted directly with maleic anhydride at a temperature
10 in the range 175 to 250 °C, preferably 190 to 235 °C, more preferably 200 to 235 °C. The molar ratio maleic anhydride : atactic propylene oligomer is advantageously in the range 1:1 to 5:1, preferably 1.2:1 to 4:1, more preferably 1.5:1 to 3.6:1.

15 The molar ratio dicarboxylic acid or anhydride moieties : atactic propylene oligomer (r) of the alkenyl-substituted dicarboxylic acid or anhydride is readily calculated from the expression:

$$20 \quad r = \frac{M_n \times AV}{(20 \times AM - AV \times 96)}$$

in which:

M_n = Number average molecular weight of the atactic propylene oligomer

25 AV = Acid value of the reaction product (mmol/g)

AM = Active matter in the reaction product (%m)

"Active matter" denotes propylene oligomer bearing carboxylic acid groupings, from which it will be understood that the unreacted nonpolar polyolefins do
30 not contribute to the AM.

Preferably, the molar ratio dicarboxylic acid or anhydride acid moieties : atactic propylene oligomer is in the range of 1:1 to 1.5:1, more preferably 1:1 to 1.3:1.

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It is preferred that at least 90%w, preferably at least 95%w, of the atactic propylene oligomer is of formula I.

Number average molecular weight (M_n) and weight average molecular weight (M_w) can be determined by gel permeation chromatography, with suitable calibration, in order to determine the ratio M_w/M_n , which is a measure indicating the width of molecular weight distribution. M_w/M_n values for polyolefins typically fall in the range 1.5 to 4.0. For the atactic propylene oligomers from which the ester derivatives of the present invention are prepared, M_w/M_n determined by gel permeation chromatography is preferably 2.5 or less, more preferably 2 or less.

The alkenyl-substituted dicarboxylic acid or anhydride derivatives of the present invention find their prime application as additives for lubricating oil compositions, although they may be incorporated in hydrocarbon fuels such as gasolines.

Accordingly, the present invention further provides a lubricating oil composition which comprises a major proportion (more than 50%w) of a lubricating oil and a minor proportion, preferably from 0.1 to 10%w, especially 0.5 to 5%w, based on the total composition, of a derivative as defined hereinabove.

The lubricating oil composition may suitably comprises a mixture of derivatives containing different polyether polyol groups.

The lubricating oil used in such compositions can be natural, mineral or synthetic in origin. Natural lubricating oils include animal and vegetable oils, such as castor oil. Mineral oils comprise the lubricating oil fractions derived from crude oils, coal or shale, which fractions may have been subjected to certain treatments such as clay-acid, solvent or hydrogenation treatments. Synthetic lubricating oils

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include synthetic polymers of hydrocarbons, modified alkylene oxide polymers, and ester lubricants, which are known in the art. These lubricating oils are preferably crankcase lubricating oils for spark-
5 ignition and compression-ignition engines, but include also hydraulic lubricants, metal-working fluids and automatic transmission fluids. The lubricating oil composition in accordance with the present invention may contain various other additives, known in the art,
10 such as viscosity index improvers, e.g. linear or star-shaped polymers of a diene such as isoprene or butadiene, or a copolymer of such a diene with optionally substituted styrene. These copolymers are suitably block copolymers and are preferably
15 hydrogenated to such an extent as to saturate most of the olefinic unsaturation. Other suitable additives include dispersant V.I. improvers such as those based on block copolymers, or polymethacrylates, extreme pressure/anti-wear additives such as zinc or sodium
20 dithiophosphates, anti-oxidants, friction modifiers or metal-containing detergents such as phenates, sulphonates, alkylsalicylates or naphthenates, all of which detergents may be overbased.

The lubricating oil composition according to the
25 present invention has excellent dispersancy properties.

The lubricating oil composition according to the present invention is suitably prepared by blending an additives concentrate into the lubricating base oil. Such concentrate generally comprises a lubricating oil
30 as solvent/diluent and one or more additives in a concentrated form. Hence, the present invention further provides a lubricating oil concentrate comprising a lubricating oil and a polyolefin-substituted dicarboxylic acid or anhydride derivative as described
35 hereinabove, in an amount of 10 to 80%w based on the total concentrate.

The invention will now be illustrated by means of the following Examples.

Example 1

An atactic propylene oligomer (APO) (Mn 835) was prepared by a method analogous to that disclosed in Examples 1 to 4 of EP-B-0490454. The atactic propylene oligomer (21.37 kg, 25.23 mol) and maleic anhydride (MALA) (4.63 kg, 47.24 mol) were heated together at reflux temperature (225 °C) in a glass reactor equipped with baffles, turbine stirrer, reflux condenser, nitrogen inlet, temperature probe and electrical heating mantle for 4 hours. Unreacted MALA was removed by vacuum distillation. The residue was then allowed to cool to ambient temperature (20 °C), diluted with heptane to about 50% w and insoluble matter was removed by filtration. The heptane was then evaporated off yielding a clear, light yellow viscous liquid product (25.0 kg) which was found to have active matter content of 77.9 %w and acid value 1.87 milli-equivalents/g (meq/g). This analysis data indicates a succination ratio of 1.14:1 mol MALA/ mol propylene oligomer.

Active matter content was determined by separating inactive material from the desired active matter on an aluminium oxide column using diethyl ether as eluant (AMS 807). Acid value was determined by potentiometric titration with aqueous potassium hydroxide of a weighed amount of product dissolved in a toluene/methyl ethyl ketone/t-butanol/water mixture (SMS 2746). Results are given in Table 1.

Example 2

A mixture of 2.5 kg (2.66 mol) polyisobutylene (PIB) (Mn 950) and 391 g (3.99 mol) of maleic anhydride (MALA), yielding a molar ratio of maleic anhydride to polyisobutylene of 1.5:1, was heated to 235 °C over 4 hours. The excess maleic anhydride was removed by evaporation under reduced pressure yielding a product

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which was found to have active matter content of 67.8 %w and acid value 1.52 milli-equivalents/g (meq/g). This analysis data indicates a succination ratio of 1.2:1 mol MALA/ mol polyisobutylene.

5 Results are given in Table 1.

Example 3

The APO-MALA product (51.55 g, 0.062 mol) obtained in Example 1, 47 g of a HVI 60 oil and pentaerythritol (PENTA) (10.94 g, 0.08 mol) were heated at 200 °C for 12
10 hours in an autoclave. The product so obtained was a clear dispersant which was found to have active matter content of 50.0 %w and acid value 0.08 milli-equivalents/g (meq/g). This analysis data indicates an esterification ratio of 1:1.3 mol APO-MALA/ mol PENTA.
15 Results are given in Table 1.

Example 4

The PIB-MALA product (121.0 g, 0.066 mol) obtained in Example 2 was subjected to a similar process as described in Example 3, except that 11.75 g (0.086 mol)
20 PENTA was used. The resultant reaction mixture was then heated at 200 °C for 12 hours in an autoclave. The product obtained was a clear dispersant which was found to have active matter content of 67.2 %w and acid value 0.08 milli-equivalents/g (meq/g). This analysis data
25 indicates an esterification ratio of 1:1.3 mol PIB-MALA/ mol PENTA. Results are given in Table 1.

Example 5

The APO-MALA product (70.0 g, 0.065 mol) obtained in Example 1 was reacted at 160 °C with tri-ethylene tetramine (TETA) (56.7 g, 0.36 mol) at an APO-MALA to
30 amine ratio of 1:0.55 for about 4 hours. The reaction mixture was then filtered to yield the desired product, which was found to have active matter content of 78.7 %w and acid value 0.02 meq/g.

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Example 6

The products of Examples 3 to 5 and a commercially available PIB-MALA-TETA composition were each diluted to an active matter content of 50%w by addition of "HVI 5 60" base oil (a bright and clear high viscosity index base oil having viscosity at 100 °C 4.4 to 4.9 mm²/s (ASTM D 2270)). The resulting concentrates were then tested as follows:

Carbon Black Dispersancy Test (CBDT) (British Rail 10 publication BR 669 : 1984)

Samples of a SAE 15W40 Middle East lubricating oil containing a commercial package of a zinc dialkyldithiophosphate, an overbased calcium alkyl salicylate and VI improver, were modified by 15 incorporation of concentrate to give oils containing the products of Examples 3 to 5 and the commercially available PIB-MALA-TEPA composition at a concentration of 1%w active matter. 3%w of carbon black was then added to each oil and (percentage) increase in 20 kinematic viscosity at 60 °C was determined using an Ubbelohde viscometer. A low result is an indication of less sludge forming in engines and indicates therefore good dispersant performance.

The results are shown in Table 2. It will be clear 25 from Table 2 that the composition according to the present invention (Example 3) performs much more attractively than conventional compositions falling just outside the scope of the present invention (Examples 4 to 5, and the commercially available 30 PIB-MALA-TEPA composition).

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Table 1

Product of Ex.	Product		
	Active matter (%w)	Acid value (meg/g)	Succ/ester. Ratio
1	77.9	1.87	1.14:1
2	67.8	1.52	1.20:1
3	50.0	0.08	1.3:1
4	67.2	0.08	1.3:1
5	78.7	0.02	-

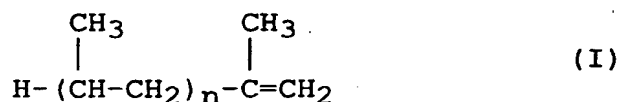
Table 2

Product of Example	CBDT (%)
3	32.0
4	37.0
5	45.1
*	46.3

* the commercially available PIB-MALA-TETA composition

C L A I M S

1. An alkenyl-substituted dicarboxylic acid or anhydride ester derivative, useful as dispersant additive in lubricating oil compositions, having an alkenyl group derived from an atactic propylene oligomer substantially of the formula

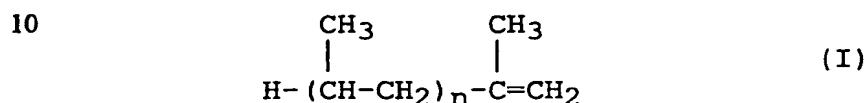


- where n is in the range 15 to 120, having number average molecular weight (M_n) in the range 700 to 5000, and molar ratio dicarboxylic acid or anhydride moieties : atactic propylene oligomer in the range 1:1 to 2:1, and having an ester group derived from a polyol.
2. An ester derivative according to claim 1, wherein the alkenyl group is derived from an atactic propylene oligomer of formula I which has n in the range 15 to 70 and M_n in the range 700 to 3000.
3. An ester derivative according to claim 1 or 2, wherein the polyol is an alkane polyol having at least two hydroxy groups.
4. An ester derivative according to claim 3, wherein the alkane polyol is pentaerythritol, glycerol, sorbitol or sucrose, or a mixture of two or more thereof.
5. An ester derivative according to any one of claims 1 to 4, wherein the molar ratio dicarboxylic acid or anhydride groups to polyol groups is in the range 0.5:1 to 10:1.
6. An ester derivative according to any one of claims 1 to 5, wherein at least 95%w of the atactic propylene oligomer is of formula I.

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7. An ester derivative according to any one of claims 1 to 6, wherein the value M_w/M_n of the atactic propylene oligomer determined by gel permeation chromatography is 2.5 or less.

- 5 8. A process for preparing an ester derivative according to any one of claims 1 to 7 which comprises reacting an alkenyl-substituted dicarboxylic acid or anhydride having an alkenyl group derived from an atactic propylene oligomer substantially of the formula



where n is in the range 15 to 120, having number average molecular weight (M_n) in the range 700 to 5000, and molar ratio dicarboxylic acid or anhydride
15 moieties : atactic propylene oligomer in the range 1:1 to 1.5:1, with a polyol.

9. A process according to claim 8, wherein the molar ratio alkenyl-substituted dicarboxylic acid or
20 anhydride to polyol is in the range of 0.5:1 to 10:1.
10. A lubricating oil composition which comprises a major proportion of a lubricating oil and a minor proportion of an ester derivative as claimed in any one of claims 1 to 7.
- 25 11. A lubricating oil concentrate which comprises a lubricating oil and 10 to 80%w, based on the total concentrate, of an ester derivative as claimed in any one of claims 1 to 7.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 96/03977

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C69/53 C07C57/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 490 454 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 17 June 1992 cited in the application see page 3, line 11 - page 4, line 6 see page 5, line 43 - page 7, line 37 see page 11, line 35 - line 53 see claims 1,14	1
Y	GB,A,1 483 729 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 24 August 1974 see page 1, line 64 - line 80 see page 2, line 90 - page 3, line 4 see page 3-4; example 1 see claims 1-17	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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